

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

United States Patent and Trademark
Office
(Box PCT)
Crystal Plaza 2
Washington, DC 20231
ÉTATS-UNIS D'AMÉRIQUE

in its capacity as elected Office

Date of mailing (day/month/year) 24 March 1999 (24.03.99)	
International application No. PCT/US98/14775	Applicant's or agent's file reference NCI 6738WO
International filing date (day/month/year) 16 July 1998 (16.07.98)	Priority date (day/month/year) 17 July 1997 (17.07.97)
Applicant THORPE, Allen, W. et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:

05 February 1999 (05.02.99)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

<p>The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland</p> <p>Facsimile No.: (41-22) 740.14.35</p>	<p>Authorized officer</p> <p>Christelle Croci</p> <p>Telephone No.: (41-22) 338.83.38</p>
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/14775

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C03C 25/06; B60K 15/03; B65D 1/00, 6/34

US CL : Please See Extra Sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 428/34.5, 36.1, 290, 365, 410, 428; 216/97, 108; 220/645; 264/257; 523/214; 524/494

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS; e glass, sulfuric acid, leach###, intumescen###, polyolefin, silicone oil, fuel tank, flame retardan##, emulsion, layer##, mold###

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ---- Y	US 5,020,687 A (SEIZERT) 04 June 1991 (04-06-91), column 3, lines 51-59 and figures.	16-24 ----- 10-24, 28-33, 35, 36, 41-47
X ---- Y	US 4,063,001 A (ZLOCHOWER) 13 December 1977 (13-12-77), column 2, lines 6-21.	16-24, 28-33 ----- 1-8, 10-24, 28-36, 41-47
X	US 3,692,186 A (MARZOCCHI) 19 September 1972 (19-09-72), column 4, line 45 to column 5, line 2 and column 6, lines 14-15.	1-5

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier document published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	
"P"	document published prior to the international filing date but later than the priority date claimed	"A" document member of the same patent family

Date of the actual completion of the international search

01 OCTOBER 1998

Date of mailing of the international search report

28 OCT 1998

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

TAE H. YOON

Telephone No. 703-308-0661

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/14775

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RAMACHANDRAN et al, Studies on the Acid resistance of E Glass, Journal of the American Ceramic Society, January 1980, Vol 63, pages 1-3.	1-5
X	US 2,992,960 A (LEEG et al) 18 July 1961 (18-07-61), examples 2 and 22.	1-7, 28-33
X	US 4,529,467 A (WARD et al) 16 July 1985 (16-07-85), column 6, line 66 to column 7, line 7.	34
X ----- Y	US 5,258,159 A (FREEMAN et al) 02 November 1993 (02-11-93), abstract and column 2, lines 5-22.	16-18, 23-26 ----- 10-31, 33, 35, 36, 41-47
X	US 5,308,571 A (STILES et al) 03 May 1994 (03-05-94), abstract, column 2, lines 5-14 and column 7, lines 10-20.	16-18, 22-24
X	US 5,334,427 A (COGNET et al) 02 August 1994 (02-08-94), column 2, line 42 to column 3, line 9 and example 1.	48-50
Y	US 5,242,744 A (SCHRYER) 07 September 1993 (07-09-93), column 3, lines 27-55.	8, 10, 27, 34, 35, 41, 48
Y	US 3,849,178 A (FELDMAN) 19 November 1974 (19-11-74), column 1, lines 39-40.	10, 27, 34, 35, 41, 48
Y	US 2,491,761 A (PARKER et al) 20 December 1949 (20-12-49), column 2, lines 47-60 and example 2.	1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/14775

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

428/34.5, 36.1, 290, 365, 410, 428; 216/97, 108; 220/645; 264/257; 523/214; 524/494

PATENT COOPERATION TREATY

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To: POLSTER, J. PHILIP
POLSTER, LIEDER, WOODRUFF & LUCCHESI
763 SOUTH NEW BALLAS ROAD
ST. LOUIS, MISSOURI 63141

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NOTIFICATION OF TRANSMITTAL OF INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Rule 71.1)

Applicant's or agent's file reference NCI 6738WO		IMPORTANT NOTIFICATION	
International application No. PCT/US98/14775	International filing date (day/month/year) 16 JULY 1998	Priority Date (day/month/year) 17 JULY 1997	
Applicant NU-CHEM, INC.			

Date of Mailing
(day/month/year)

15 JUL 1999

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.
4. **REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices)(Article 39(1))(see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer TAE H. YOON Telephone No. 703-308-0661
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference NCI 6738WO	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/US98/14775	International filing date (day/month/year) 16 JULY 1998	Priority date (day/month/year) 17 JULY 1997
International Patent Classification (IPC) or national classification and IPC Please See Supplemental Sheet.		
Applicant NU-CHEM, INC.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 4 sheets.
- ☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority. (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).
- These annexes consist of a total of 5 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of report with regard to novelty, inventive step or industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☐ Certain observations on the international application

Date of submission of the demand 05 FEBRUARY 1999	Date of completion of this report 30 JUNE 1999
Name and mailing address of the IPEA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231	Authorized officer <i>TAE H. YOON</i> Telephone No. 703-308-0661
Facsimile No. (703) 305-3230	

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No.

PCT/US98/14775

I. Basis of the report

1. This report has been drawn on the basis of *(Substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments):*

☐ the international application as originally filed.

☒ the description, pages (See Attached) , as originally filed.

pages _____ , filed with the demand.

pages _____ , filed with the letter of _____.

pages _____ , filed with the letter of _____.

☒ the claims, Nos. (See Attached) , as originally filed.

Nos. _____ , as amended under Article 19.

Nos. _____ , filed with the demand.

Nos. _____ , filed with the letter of _____.

Nos. _____ , filed with the letter of _____.

☒ the drawings, sheets/fig (See Attached) , as originally filed.

sheets/fig _____ , filed with the demand.

sheets/fig _____ , filed with the letter of _____.

sheets/fig _____ , filed with the letter of _____.

2. The amendments have resulted in the cancellation of:

☒ the description, pages NONE.

☒ the claims, Nos. NONE.

☒ the drawings, sheets/fig NONE.

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the ~~Supplemental Box~~ Additional observations below (Rule 70.2(c)).

4. Additional observations, if necessary:

NONE

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**1. STATEMENT**

Novelty (N)	Claims <u>1-53</u>	YES
	Claims <u>NONE</u>	NO
Inventive Step (IS)	Claims <u>1-9, 21, 25-34, 37-48</u>	YES
	Claims <u>10-20, 22-24, 35, 36, 49-53</u>	NO
Industrial Applicability (IA)	Claims <u>1-53</u>	YES
	Claims <u>NONE</u>	NO

2. CITATIONS AND EXPLANATIONS

Claims 10-20, 22-24, 35, 36 and 49-53 lack an inventive step under PCT Article 33(3) as being obvious over FREEMAN et al in view of HORROCKS et al. FREEMAN does not teach a precoated fabric of the instant invention, however, the use of precoated fibrous reinforcing material with subliming materials or intumescent compositions is routine as taught by HORROCKS et al (column 3, lines 41-48 and column 4, lines 15-27). Thus, it would be obvious to precoat fiberglass fabrics of FREEMAN with flame retardant materials of HORROCKS et al. Contrary to applicant's assertion, said column 4 clearly teaches reinforcing inorganic fibers. Argument based on the prior art which is not on the record has no probative value.

Claims 10-20, 22-24, 35, 36 and 49-53 lack an inventive step under PCT Article 33(3) as being obvious over SEIZERT in view of HORROCKS et al. SEIZERT does not teach a precoated fabric of the instant invention, however, the use of precoated fibrous reinforcing material with subliming materials is routine as taught by HORROCKS et al (column 3, lines 41-48 and column 4, lines 15-27). Thus, it would be obvious to precoat fiberglass fabrics of SEIZERT with flame retardant materials of HORROCKS et al. Contrary to applicant's assertion, said column 4 clearly teaches reinforcing inorganic fibers.

Claims 1-53 meet the criteria set out in PCT Article 33(4), because the instant acid-treated fiberglass is useful in making composite materials such as fuel tank or trunk base.

Claims 1-53 meet the criteria set out in PCT Article 33(2), because the prior art does not teach or fairly suggest the instant acid treatment of fiberglass and a precoating thereon.

Claims 1-9, 21, 25-34 and 37-48 meet the criteria set out in PCT Article 33(3), because the prior art does not teach or fairly suggest the instant acid treatment and emulsion coating.

_____ NEW CITATIONS _____

Supplemental Box

(To be used when the space in any of the preceding boxes is not sufficient)

Continuation of: Boxes I - VIII

Sheet 10

CLASSIFICATION:

The International Patent Classification (IPC) and/or the National classification are as listed below:

IPC(6): C03C 25/06; B60K 15/03; B65D 1/00, 6/34 and US Cl.: 428/34.5, 36.1, 290, 365, 410, 428, 921; 216/97, 108; 220/645; 264/257; 523/214; 524/494

I. BASIS OF REPORT:This report has been drawn on the basis of the description,
pages, 1-16, as originally filed.

pages, NONE, filed with the demand.

and additional amendments:

NONE

This report has been drawn on the basis of the claims,
numbers, NONE, as originally filed.

numbers, NONE, as amended under Article 19.

numbers, NONE, filed with the demand.

and additional amendments:

Claims 1-53, filed with the letter of 28 June 1999.

This report has been drawn on the basis of the drawings,
sheets, 1, as originally filed.

sheets, NONE, filed with the demand.

and additional amendments:

NONE

Claims

1. A method of treating fiberglass fiber to increase its resistance to heat, the method comprising treating the fiber with a mixture of acids comprising at least 15% sulfuric acid for a period sufficient to increase the softening point of the fiber to at least 1000° C.
2. The method of claim 1 wherein the fiber is formed into a fabric before it is treated.
3. The method of claim 2 wherein the acid mixture further comprises at least one other mineral acid.
4. The method of claim 3 wherein the acid mixture comprises hydrochloric acid.
5. The method of claim 1 wherein the fiber is E-glass.
6. The method of claim 1 wherein the fiber is soaked in an acid bath for a period in excess of twenty-four hours.
7. The method of claim 2 comprising a further step of treating the fabric with a low viscosity resin after the acid treatment step.
8. The method of claim 7 wherein the resin is a silicone oil.
9. The method of claim 8 wherein the silicone oil is a water in oil emulsion.
10. A composite material comprising at least one layer containing a thermoplastic, the layer having embedded therein a fabric, the fabric being coated with an active thermal protective material selected from the group consisting of subliming materials and intumescent materials.
11. The composite of claim 10 wherein the coated fabric comprises an open mesh having from 0.5 to 30 openings per square centimeter, the thermoplastic in the layer extending into the openings and forming a mechanical lock with the coated fabric.
12. The composite of claim 10 wherein the fabric comprises fiberglass fiber having a softening point above about 850° C.

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13. The composite of claim 10 wherein the active thermal protective material leaves openings in the weave of the fabric, the thermoplastic material extending into the openings and forming a physical lock with the coated fabric.
14. A container formed of the composite of claim 10.
- 5 15. The container of claim 14 wherein the container is a structural automotive container selected from the group consisting of trunk bases and fuel tanks.
16. A structural automotive component having a bottom and an upstanding wall, the pan being formed of the composite material of claim 10.
- 10 17. The component of claim 16 wherein the mesh is on a lower side of the bottom and the outside of the upstanding wall.
18. The component of claim 17 wherein the fabric mesh is a single piece of material extending across the bottom and up at least a part of the upstanding wall.
- 15 19. The component of claim 16 wherein the fabric comprises fiberglass fiber having a softening point above about 850° C.
20. The component of claim 19 wherein the fabric comprises fiberglass fiber having a softening point above about 1000° C.
21. The component of claim 20 wherein the fabric has been treated with a
- 20 mixture of acids comprising at least 15% sulfuric acid.
22. The component of claim 16 wherein the component is a trunk base.
23. The component of claim 16 wherein the component is a fuel tank.
24. The component of claim 16 wherein the component is an inverted pan formed in part of thermoplastic-coated fibers, the fabric mesh being embedded
- 25 in an inside surface of the pan.
25. A method of forming a composite structure comprising a step of coating a fabric with an active thermal protective material selected from the group consisting of subliming and intumescent materials, and thereafter a step of softening a resin component of a substrate and embedding the coated fabric in
- 30 the softened resin.

26. The method of claim 25 wherein the substrate is a sheet, and wherein the sheet and the fabric are formed into a structure simultaneously with the step of embedding the fabric in the sheet.
27. The method of claim 25 wherein the active thermal protective material
5 leaves openings in the weave of the fabric, the softened resin extending into the openings and forming a physical lock with the coated fabric.
28. A composite material comprising at least one layer of thermoplastic having embedded therein a fabric produced by the method of claim 2.
29. A composite material comprising at least one layer of thermoplastic
10 having embedded therein fibers produced by the method of claim 1.
30. A thermal protective composition having dispersed therein fibers produced by the method of claim 1.
31. In combination, a thermal protective material and a fiberglass fabric embedded therein, the fabric having been treated by the method of claim 2.
- 15 32. The combination of claim 31 wherein the thermal protective material is a coating applied to a substrate.
33. The combination of claim 31 wherein the thermal protective composition is preformed into a self-supporting structure.
34. A method of protecting a substrate from fire or thermal extremes
20 comprising applying to the substrate an uncured thermal protective material selected from the group consisting of intumescent materials and subliming materials, and thereafter a step of embedding in the thermal protective material a fiberglass fabric produced by the method of claim 2.
35. A structure comprising an organic resin having embedded therein a
25 fabric, the fabric being precoated with an active thermal protective material selected from the group consisting of subliming and intumescent materials.
36. The structure of claim 35 wherein the organic resin is a polyolefin.
37. A method of treating fiberglass fiber to give it superior high temperature resistance and texture, the method comprising treating the fiber with acid and

thereafter soaking the fiber in a water-in-oil emulsion of low viscosity organo-metallic oil to fill pores in the glass.

38. The method of claim 37 wherein the low viscosity organo-metallic oil is a low molecular weight silicone oil.
- 5 39. The method of claim 38 wherein the silicone is dimethyl polysiloxane.
40. The method of claim 37 wherein the step of treating the fiber with acid comprises treating the fiber with a mixture of acids comprising at least 15% sulfuric acid for a period sufficient to increase the softening point of the fiber to at least 1000° C.
- 10 41. A method of forming a composite structure comprising a step of treating a fabric with an active thermal protective material selected from the group consisting of subliming and intumescent materials, a step of placing the treated fabric in a mold, and a step of forming a substrate into a shape in the mold containing the treated fabric.
- 15 42. The method of claim 41 wherein the substrate comprises a thermoplastic resin, the step of forming the substrate comprising heating the resin at least to a softening temperature, the treated fabric bonding to the softened resin.
43. The method of claim 41 wherein the substrate is heated to a temperature below an activation temperature at which the active thermal protective material
20 intumesces or sublimes.
44. The method of claim 41 wherein the fabric comprises fiberglass.
45. The method of claim 41 wherein the substrate comprises a felted material.
46. The method of claim 41 wherein the coated fabric includes windows
25 therein, the substrate extending through the windows to lock the coated fabric to the substrate.
47. The method of claim 41 wherein the structure is an automotive trunk base, or trunk liner, or fuel tank.
48. The method of claim 41 wherein the resin comprises a polyolefin.

49. A composite structure comprising a substrate, the substrate being formed at least in part of a thermoplastic material, and a thermal protective structure adhered to the substrate, the thermal protective structure comprising a fabric coated with an active thermal protective material, the thermal protective material being selected from the group consisting of subliming and intumescent materials, the substrate adhering chemically and mechanically to the pretreated mesh fabric.
50. The structure of claim 49 wherein the thermal protective structure is adhered to the substrate by the thermoplastic material.
51. The structure of claim 49 wherein the thermal protective structure is embedded in the thermoplastic material.
52. A composite structure comprising a substrate, the substrate being formed at least in part of a polyolefin, and a mesh fabric treated with an active thermal protective material, the thermal protective material being selected from the group consisting of subliming and intumescent materials, the treated mesh fabric having from 0.5 to 30 openings per square centimeter, the resin adhering chemically and mechanically to the pretreated mesh fabric.
53. The structure of claim 52 wherein the polyolefin is polypropylene.



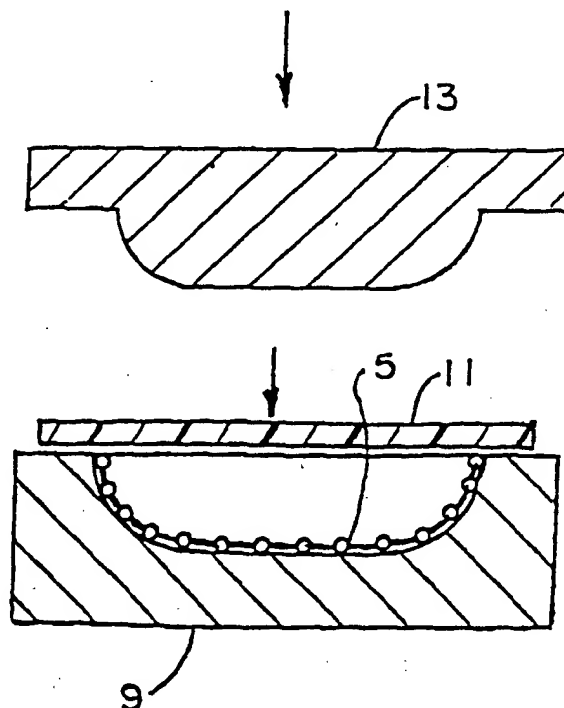
INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C03C 25/06, B60K 15/03, B65D 1/00, 6/34		A1	(11) International Publication Number: WO 99/03792
			(43) International Publication Date: 28 January 1999 (28.01.99)
(21) International Application Number: PCT/US98/14775		(74) Agent: POLSTER, J., Philip; Polster, Lieder, Woodruff & Lucchesi, 763 South New Ballas Road, St. Louis, MO 63141 (US).	
(22) International Filing Date: 16 July 1998 (16.07.98)			
(30) Priority Data: 08/895,918 17 July 1997 (17.07.97) US		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).	
(63) Related by Continuation (CON) or Continuation-in-Part (CIP) to Earlier Application US 08/895,918 (CIP) Filed on 17 July 1997 (17.07.97)			
(71) Applicant (for all designated States except US): NU-CHEM, INC. [US/US]; 2200 Cassens Drive, Fenton, MO 63026 (US).			
(72) Inventors; and (75) Inventors/Applicants (for US only): THORPE, Allen, W. [US/US]; 9458 LaJolla, Olivette, MO 63132 (US). TAYLOR, Edward, W., Jr. [US/US]; 181 Tortuna Drive, Ballwin, MO 63021 (US). FELDMAN, Rubin [US/US]; 28 Somerset Downs, Ladue, MO 63124 (US). DEOGON, Malkit, S. [GB/GB]; 23 Vicrage Road, Edgbaston, Birmingham B15 3HB (GB).		Published With international search report.	

(54) Title: METHODS OF MAKING HIGH-TEMPERATURE GLASS FIBER AND THERMAL PROTECTIVE STRUCTURES

(57) Abstract

A glass fiber capable of withstanding temperatures in excess of 1900 °F (1038 °C) is produced by treating a glass, preferably E-glass, fiber. The glass fiber is first leached with selected acids, and then the leached fiber is treated with organo-metallic materials of low viscosity, such as a dispersion of low molecular weight water-in-oil emulsion of dimethyl polysiloxane. The fiber is used in such applications as embedding it in a fire-resistant active coating material or embedding it into one surface of a polyolefin or composite plastic, such as a polypropylene sheet. The treated fiberglass can be used as a sole component or in concert with a fire-resistant or fire retardant material to further enhance its fire-resistant properties. Other fire-resistant composite materials are formed by precoating a fabric (1) with an active (intumescent or subliming) material (3), then embedding the precoated fabric (5) into a surface of a preferably thermoplastic sheet substrate (11). The precoated fabric is preferably adhered to or embedded in the surface of the substrate simultaneously with a molding process which forms the composite into a shape such as an automotive container like a fuel tank or trunk base. Other composites (21) are formed by adhering thermal protective structure (28) comprising a fabric (29) precoated with an active thermal protective composition (31) to a structure (23, 25, 27, 33) formed from fibers coated with an adhesive.



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BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
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METHODS OF MAKING HIGH-TEMPERATURE GLASS FIBER AND THERMAL PROTECTIVE STRUCTURES

Technical Field

This invention relates to a glass form, preferably a fiber, which resists
5 high temperatures, at least 1900° F. (1038° C.) and higher, while retaining at
least some of its tensile strength and other physical properties. It also relates to
structures, including automotive structures, which can resist high temperature
for a predetermined time.

Background Art

10 In numerous applications, fabrics are utilized in systems which resist
high temperatures. An example of the use of such fabrics is in reinforced
coating systems. In these systems, the fabric is embedded in a char-forming,
fire-resistive coating such as those described in Deogon, U.S. Patent No.
5,591,791. Briefly, such coatings include ablative coatings, which swell to less
15 than twice their original thickness when exposed to fire or other thermal
extremes, intumescent coatings such as those disclosed in Nielsen et al., U.S.
Patent 2,680,077, Kaplan, U.S. Patent 3,284,216, Ward et al., U.S. Patent
4,529,467, or Deogon, U.S. Patent No. 5,591,791, which swell to produce a
char more than five times the original thickness of the coating, and subliming
20 char-forming coatings of the type disclosed in Feldman, U.S. Patent 3,849,178,
which undergo an endothermic phase change and expand two to five times their
original thickness to form a continuous porosity matrix. The intumescent and
subliming coatings are denoted "active" thermal protective coatings.

The time required for a given temperature rise across a predetermined
25 thickness of the composition, under specified heat flux, environmental, and
temperature conditions, is a measure of the composition's effectiveness in
providing thermal protection to an underlying substrate.

Eventually, the char is consumed by physical erosion and by chemical
processes, such as oxidation by oxygen in the air and by free radicals produced
30 by the coating or otherwise in a fire environment, and protection is substantially

reduced. Before the char is totally consumed, degradation of the char layer leaves it crumbled and without the necessary strength to sustain itself, causing it to fail by being blown off or simply falling off (spalling).

Some of these chars degrade rapidly during exposure to high
5 temperature, high heat flux environments. In the case of coatings which swell when exposed to thermal extremes, the degradations are usually in the form of fissures which are formed in the char as a result of differential thermal stresses produced by the high thermal gradients within the char, and differential thermal expansion between the virgin material and the char.

10 To increase the strength of char layers during exposure to thermal extremes, and to limit spalling and fissures, fabrics have long been incorporated in the coating materials. As set out in Feldman et al., U.S. Patent No. 5,622,774, fiberglass fabric provides an inexpensive, easy to install, reinforcement in many high temperature applications. In certain applications,
15 however, such as coatings which may be exposed to high velocity petroleum fires or to high-temperature, high heat flux fires which will raise the fabric to temperatures above the softening point of the glass (around 1600° F., 871° C.), the fiberglass fabric has disintegrated. Other fabrics have therefore been required. Graphite cloth, as taught in the foregoing Feldman et al. U.S. Patent
20 5,622,774 and in Kobayashi et al., U.S. Patent No. 5,401,793, is very expensive. Refractory materials, such as quartz (Refrasil) fabric is also expensive. Metal mesh is inexpensive but it is heavy and difficult to install, particularly because it generally requires welding metal studs to the substrate to be protected.

Other examples of fabric-reinforced systems are laminates in which the
25 fabric is embedded directly in a structural resin material itself, for example in the structure of a furnace or a rocket nozzle. Generally, these materials also produce a char when exposed to sufficiently high temperatures, although in many applications they are routinely exposed to high temperatures below their char-forming temperature for extended periods. In other applications they are
30 exposed for short periods to temperature, heat flux, and environmental

conditions which do not cause a char to form, but which are sufficiently high to cause serious loss of structural properties. Examples of these latter systems are automobile gasoline tanks and trunks, which can be made of plastic material (generally a thermoplastic material) if they can pass a test involving preventing structural failure (such as drop through in the case of a trunk or an explosion in the case of a gasoline tank) when the trunk or tank is placed over a fire of a specified temperature and intensity for a predetermined period such as two minutes. Also, other automotive components, such as trunk liners, parcel shelves, and interior door panels, are sometimes formed of felted natural or synthetic fibers having a thermoplastic binder or substrate. In all of these conditions, a fabric which resists complete degradation under the foregoing conditions can provide sufficient structural integrity to impede failure of the system. Other approaches to providing sufficient integrity to thermoplastic automotive components and other automotive components containing thermoplastic binders are also needed.

Attempts have been made for many years to produce a glass fiber which retains a substantial portion of its mechanical properties even when subjected to very high temperatures, greater than 1600° F. (871°C.), and preferably on the order of 1900° to 2000° F. (1038° to 1093° C.). Examples are Nordberg, U.S. Patent No. 2,461,841, Parker et al., U.S. Patent No. 2,491,761, and Leeg et al., U.S. Patent No. 2,992,960. These patents all involve leaching of the glass fiber with mineral acid, followed by treatment with a sizing material. Heretofore, such attempts have failed to provide a reliable, reproducible, and efficient process of converting commercial grade fiberglass (such as Type E and Type F glass fibers) into a material capable of withstanding elevated temperatures and aerodynamic shear which may be coupled with elevated temperatures.

Likewise, no economical, simple means is known for protecting thermoplastic and thermoplastic-containing structures, such as automotive components from high temperatures.

30 Summary of Invention

In accordance with one aspect of the present invention, generally stated, a method of making a heat-resistant fiberglass fabric is provided comprising soaking a fiberglass fabric in a carefully selected acid bath for a selected time at a selected temperature. We have found that soaking the fiberglass in a mixture
5 of acids containing at least 15% sulfuric acid at room temperature for a period of more than twenty-four hours, preferably at least about forty-eight hours, produces a material which maintains a substantial part of its physical characteristics even when heated to a temperature of at least 1600° F. (871° C.) for a period of at least one hour. The molality of the mixed acids is below 8,
10 preferably around 5. It is anticipated that shorter soak times may be achieved with higher temperatures.

We have also found that the acid-treated fiberglass can be given superior qualities, such as improved "hand" (texture) both before and during exposure to high temperatures, by soaking the fiberglass in a low viscosity organo-metallic
15 material, such as a low molecular weight silicone to fill the pores of the glass. The silicone is preferably in the form of a water-in-oil emulsion of low molecular weight silicone, such as dimethyl polysiloxane. The use of a water-in-oil emulsion, rather than an oil-in-water emulsion, inhibits the formation of silicone micelles and enhances absorption of the silicone into the pores of the
20 glass fibers. We have found that soaking a fiberglass fabric for a period of more than forty-eight hours, preferably at least seventy-two hours, at room temperature in a low molecular weight, low viscosity, silicone bath produces superior results.

Certain combinations of acid treatment and treatment with low
25 molecular weight silicone have been found to produce materials which consistently will withstand being heated to a temperature of 1900° F. (1038° C.) for at least one hour in a muffle furnace.

The improved fabric has numerous uses, as will be apparent to those skilled in the art. It provides a superior reinforcement in thermal protective
30 coating systems of the types previously described. For example, it may be

embedded in fire-protective coatings of subliming, intumescent and ablative types, and has been found to provide excellent results as a reinforcement in sprayed-on subliming coating systems. It may also be used in active or passive cast or molded self-supporting thermal protective systems such as the system
5 described in Feldman, U.S. Patent No. 4,493,945.

In accordance with another aspect of the invention, structural members formed of thermoplastic resins are strengthened and protected from fire for extended periods by incorporating in them a high-temperature fiberglass fabric made in accordance with the present invention. The fabric is preferably pressed
10 into a resin sheet as the sheet is formed into a container or other functional entity.

In accordance with another aspect of the present invention, generally stated, members formed at least in part of thermoplastic resins are strengthened and protected from fire or other hyperthermal conditions for extended periods
15 by incorporating in them a fabric or mesh which is pretreated with an active (intumescent or subliming) thermal protective coating material and then embedded in the thermoplastic material. The fabric is preferably a high-temperature fiberglass made by the method of the aforementioned parent application, although other fabrics including ordinary fiberglass, other inorganic
20 materials, synthetic polymeric materials and natural organic materials such as cotton may also be used. Preferably, the fabric comprises an open weave mesh having from 0.5 to 30 openings per square centimeter. The active fire retardant material can be impregnated into the fabric material or surface coated on the fabric. Preferably, a coating of from 100 to 1,000 grams per square meter is
25 applied. It can be completely cured in a rigid or elastic form; it can also be supplied in a precured condition or in a semi-cured condition to be cured during processing. The cells of the treated or impregnated fiberglass can be preferably open or may be filled. For some materials such as polypropylene, an open cell is preferred as it enables the softened polypropylene to pass through the opening
30 and form a mechanical lock. The pretreated fabric is preferably embedded in or

bonded to a surface of the substrate, generally the surface which is expected to be exposed directly to a flame or other hyperthermal condition.

In accordance with a method of the invention, a composite structure is formed by pretreating a fabric with an active thermal protective material, placing the pretreated fabric in a mold, and bonding the pretreated fabric to a substrate while the substrate is being formed in the mold. In a preferred embodiment, the substrate is formed at least partly of a thermoplastic resin such as a polyolefin which is heated to a softening temperature and which adheres chemically and mechanically to the pretreated fabric in the mold during its molding process.

Brief Description of Drawing

FIG. 1 is a fragmentary top plan view of a thermal protective structure for use in practicing certain aspects of the present invention.

FIG. 2 is a view in side elevation thereof.

FIG. 3 is a somewhat diagrammatic sectional view showing a step in molding a composite container incorporating the structure of FIGS. 1 and 2 in accordance with one aspect of the present invention.

FIG. 4 is a somewhat diagrammatic sectional view, corresponding to FIG. 3, showing another step in the process.

FIG. 5 is a somewhat diagrammatic sectional view of the composite container formed in the process of FIGS. 3-4.

FIG. 6 is an exploded view showing the layers of a composite formed in accordance with another aspect of the present invention.

Best Modes for Carrying Out the Invention

To determine the effect of different acid compositions and exposure times at a constant temperature and acid molality, and to determine the effect of further treatment in a low molecular weight polysiloxane at a constant temperature for different time periods, a series of tests was made. The results of these tests are shown in Table 1.

Table 1

Sample No.	Acid Bath Mole Ratio Cl NO ₃ SO ₄	Time in Bath Hr.	Wt Change %	Time in Silicone Hr.	Wt Change		Wt Change		Comments
					From orig	From acid	In muffle	From orig.	
Blank							-12.44%	-12.44%	shrunk, melted
A-1	1 1 1	3	-0.08%	0	-0.08%	0.00%	-11.76%	-11.83%	fragile, crisp
A-2	1 1 1	3	-0.77%	6	5.82%	6.64%	-16.89%	-12.05%	slightly fragile
A-3	1 1 1	3	-0.34%	24	6.28%	6.63%	-17.40%	-12.22%	slightly fragile
A-4	1 1 1	3	0.00%	72	7.68%	7.68%	-17.38%	-11.04%	slightly fragile
A-5	1 1 1	8	-0.30%	0	-0.22%	0.08%	-13.80%	-13.98%	less fragile
A-6	1 1 1	8	-0.69%	6	5.66%	6.39%	-17.24%	-12.55%	less fragile
A-7	1 1 1	8	-0.35%	24	7.51%	7.89%	-18.56%	-12.44%	less fragile
A-8	1 1 1	8	-0.60%	72	7.01%	7.64%	-17.37%	-11.58%	very nice
A-9	1 1 1	24	-2.92%	0	-2.93%	-0.10%	-17.81%	-20.21%	less fragile
A-10	1 1 1	24	-3.88%	6	2.84%	6.83%	-21.10%	-18.86%	less fragile
A-11	1 1 1	24	-1.92%	24	6.92%	8.97%	-20.33%	-14.81%	less fragile
A-12	1 1 1	24	-2.12%	72	0.18%	2.30%	-20.07%	-19.92%	nice
A-13	1 1 1	48	-6.59%	0	-6.15%	0.04%	-23.14%	-27.86%	very nice - fuzzy
A-14	1 1 1	48	-7.04%	6	3.91%	11.22%	-26.89%	-24.03%	soft - fuzzy
A-15	1 1 1	48	-6.38%	24	3.98%	10.62%	-26.33%	-23.39%	very nice - fuzzy
A-16	1 1 1	48	-4.54%	72	-3.38%	1.00%	-26.16%	-28.66%	very nice - fuzzy
B-1	2 3 1	3	-0.25%	0	-0.27%	-0.02%	-10.58%	-10.82%	fragile
B-2	2 3 1	3	-0.39%	6	6.86%	7.28%	-14.91%	-9.07%	fragile
B-3	2 3 1	3	0.02%	24	6.01%	5.98%	-18.29%	-13.38%	fragile
B-4	2 3 1	3	-0.32%	72	7.62%	7.97%	-16.37%	-10.00%	less fragile
B-5	2 3 1	8	-0.85%	0	-0.79%	0.05%	-13.56%	-14.24%	fragile
B-6	2 3 1	8	-0.95%	6	4.26%	5.25%	-17.62%	-14.11%	less fragile
B-7	2 3 1	8	-1.10%	24	5.56%	6.71%	-15.79%	-11.11%	nice
B-8	2 3 1	8	-0.85%	72	5.48%	6.38%	-18.26%	-13.78%	slightly fragile
B-9	2 3 1	24	-5.47%	0	-5.27%	-0.10%	-16.44%	-20.85%	less fragile
B-10	2 3 1	24	-3.24%	6	1.86%	5.16%	-20.06%	-18.56%	nice
B-11	2 3 1	24	-4.40%	24	4.70%	9.31%	-20.89%	-17.18%	less fragile
B-12	2 3 1	24	-4.31%	72	0.79%	5.14%	-20.59%	-19.96%	nice
B-13	2 3 1	48	-10.86%	0	-9.58%	0.23%	-19.86%	-27.54%	very nice-fuzzy
B-14	2 3 1	48	-10.29%	6	1.02%	11.42%	-24.77%	-24.00%	nice - fuzzy
B-15	2 3 1	48	-9.63%	24	3.29%	13.24%	-24.99%	-22.52%	nice - fuzzy
B-16	2 3 1	48	-10.89%	72	-0.31%	10.54%	-24.76%	-24.99%	nice - fuzzy
C-1	4 2 1	3	-0.09%	0	-0.10%	-0.01%	-13.10%	-13.19%	fragile
C-2	4 2 1	3	0.00%	6	5.52%	5.52%	-16.48%	-11.87%	slightly fragile
C-3	4 2 1	3	-0.15%	24	7.62%	7.78%	-16.79%	-10.45%	less fragile

C-4	4 2 1	3	-0.08%	72	7.30%	7.39%	-18.17%	-12.20%	slightly fragile
C-5	4 2 1	8	-0.94%	0	-0.85%	0.07%	-13.07%	-13.81%	slightly fragile
C-6	4 2 1	8	-1.04%	6	4.57%	5.66%	-18.14%	-14.40%	less fragile
C-7	4 2 1	8	-0.67%	24	4.30%	4.99%	-18.83%	-15.34%	slightly fragile
C-8	4 2 1	8	-0.53%	72	4.78%	5.34%	-19.15%	-15.28%	slightly fragile
C-9	4 2 1	24	-4.83%	0	-4.63%	-0.02%	-16.68%	-20.54%	less fragile
C-10	4 2 1	24	-5.38%	6	1.54%	7.00%	-18.95%	-17.70%	slightly fragile
C-11	4 2 1	24	-5.18%	24	3.98%	9.36%	-19.70%	-16.50%	less fragile
C-12	4 2 1	24	-4.62%	72	1.52%	6.21%	-19.55%	-18.32%	less fragile
C-13	4 2 1	48	-11.42%	0	-	0.17%	-18.76%	-26.96%	nice
					10.10%				
C-14	4 2 1	48	-11.08%	6	1.59%	12.85%	-23.59%	-22.38%	less fragile
C-15	4 2 1	48	-10.30%	24	4.90%	15.71%	-25.06%	-21.38%	less fragile
C-16	4 2 1	48	-10.51%	72	0.06%	10.57%	-22.90%	-22.85%	less fragile
D-1	1 1 4	3	8.87%	0	1.78%	-7.24%	-15.64%	-14.14%	slightly fragile
D-2	1 1 4	3	1.56%	6	10.81%	9.08%	-17.73%	-8.84%	slightly fragile
D-3	1 1 4	3	0.88%	24	12.22%	11.23%	-16.50%	-6.30%	fragile
D-4	1 1 4	3	1.29%	72	9.14%	7.73%	-20.98%	-13.76%	fragile
D-5	1 1 4	8	1.32%	0	1.36%	0.02%	-15.18%	-14.03%	nice
D-6	1 1 4	8	0.77%	6	9.52%	8.67%	-21.82%	-14.38%	slightly fragile
D-7	1 1 4	8	0.27%	24	7.21%	6.93%	-19.01%	-13.17%	slightly fragile
D-8	1 1 4	8	0.58%	72	4.50%	3.90%	-19.29%	-15.66%	less fragile
D-9	1 1 4	24	1.45%	0	1.71%	0.24%	-18.33%	-16.93%	nice
D-10	1 1 4	24	0.63%	6	12.25%	11.54%	-22.71%	-13.25%	nice fuzzy
D-11	1 1 4	24	2.10%	24	12.89%	10.52%	-22.24%	-12.21%	nice fuzzy
D-12	1 1 4	24	2.09%	72	0.08%	-2.01%	-21.21%	-21.15%	nice
D-13	1 1 4	48	4.73%	0	8.04%	2.93%	-23.89%	-17.77%	nice
D-14	1 1 4	48	10.98%	6	18.84%	5.78%	-24.70%	-10.52%	soft fuzzy
D-15	1 1 4	48	10.92%	24	22.15%	8.80%	-24.48%	-7.75%	nice fuzzy
D-16	1 1 4	48	11.01%	72	-1.13%	-12.01%	-23.98%	-24.84%	nice fuzzy
E-1	1 0 4	3	0.29%	0	0.31%	0.02%	-11.51%	-11.23%	slightly fragile
E-2	1 0 4	3	0.54%	6	10.84%	10.25%	-18.64%	-9.82%	slightly fragile
E-3	1 0 4	3	0.46%	24	12.85%	12.33%	-18.33%	-7.84%	slightly fragile
E-4	1 0 4	3	0.56%	72	9.88%	9.27%	-21.75%	-14.02%	less fragile
E-5	1 0 4	8	2.41%	0	2.55%	0.08%	-17.69%	-15.60%	slightly fragile
E-6	1 0 4	8	2.64%	6	11.64%	8.70%	-18.82%	-9.37%	slightly fragile
E-7	1 0 4	8	3.02%	24	8.06%	4.80%	-18.54%	-11.97%	less fragile
E-8	1 0 4	8	3.49%	72	3.58%	-0.03%	-18.44%	-15.52%	slightly fragile
E-9	1 0 4	24	7.70%	0	8.08%	-0.24%	-22.04%	-15.74%	very nice
E-10	1 0 4	24	5.88%	6	14.80%	8.05%	-24.62%	-13.47%	soft fuzzy
E-11	1 0 4	24	7.78%	24	17.76%	9.78%	-24.16%	-10.69%	very nice

E-12	1 0 4	24	7.04%	72	-0.18%	-7.21%	-21.80%	-21.94%	nice fuzzy
E-13	1 0 4	48	10.58%	0	11.47%	-0.32%	-22.83%	-13.98%	soft fuzzy
E-14	1 0 4	48	8.31%	6	18.63%	8.78%	-25.45%	-11.56%	very nice fuzzy
E-15	1 0 4	48	11.11%	24	15.43%	2.62%	-25.56%	-14.07%	nice fuzzy
E-16	1 0 4	48	3.15%	72	0.37%	-2.79%	-24.33%	-24.05%	nice fuzzy
Examined E13, A15, B15, C15, D15 & E15									
E13 & E15 showed no visible differences under 30x microscope									
Weave threads of samples E13, E15 & D15 looked swollen									
These samples also had a softer "hand" and drooped more.									

In making these tests, the following procedure was followed.

An acid bath was prepared by weighing the relative quantities of acid, mixing the acid thoroughly, and adding sufficient water to obtain a 5.0 molal solution. The selection of the 5.0 concentration was arbitrary, but it has been found that molalities of 8 or above do not function as well.

Samples of the unraveled fiberglass material (Type E, J.P. Stevens Type 1353) were weighed and then totally immersed in the acid bath for the indicated number of hours.

At the completion of each individual immersion period, the fiberglass sample was removed from the acid bath, carefully washed with clean water, dried, and weighed. This weight was compared to the weight of the sample in its virgin state.

Some of the acid-treated fiberglass samples were then totally immersed in a bath of low molecular weight dimethyl polysiloxane in the form of a dispersion of water in the polysiloxane oil. The dispersion was formed from a concentrate of low molecular weight dimethyl polysiloxane in a water-in-oil emulsion, as sold by Blackhawk Specialty Products, Inc., Rock Island, Illinois, as its BSP-89W. The time spent in the silicone bath is recorded in Table 1 for each sample.

The sample was then placed in a muffle furnace which was maintained at a constant temperature of about 1600° F.(871° C.). This temperature was selected to represent a typical average temperature within a char layer which results from the exposure of a subliming or intumescent material which is

applied to a steel substrate in thicknesses that are capable of meeting relevant ASTM E-119 type fires for one, two, or more hours in duration.

The sample was kept in this environment for a period of about sixty minutes, then removed from the muffle furnace and cooled. Upon completion
5 of cooling, it was examined for embrittlement, "hand" retention, and weight loss. If the sample retained its "hand" (indicated by the word "nice" in the comments section of Table 1) then it was subjected to further tests. It will be seen from Table 1 that samples A-8, A-12 through A-16, B-7, B-10, B-11 through B-16, C-13, D-5, D-9 through D-16, and E-9 through E-16 met the
10 foregoing criterion and were tested further. All of these samples were soaked in the room temperature acid for a period in excess of three hours. All but C-13 had been soaked in a mixture including in excess of 15% sulfuric acid.

Fresh samples taken from corresponding lots as the foregoing samples were further exposed to 1600° F. (871° C.) in the muffle furnace for a period of
15 sixty minutes. After cooldown, they were again checked for "hand retention," and results recorded. The samples which were embrittled were eliminated from further testing, leaving samples A-13 through A-16, D-13 through D-16, and E-13 through E-16 to be tested further.

Fresh samples taken from corresponding item lots as the foregoing
20 samples were exposed to a muffle furnace fire at a temperature of about 1900° F to about 2000° F (1038°-1093° C.) for a period of one hour. This temperature was selected because it represents a thermal environment most likely encountered within the char layer of a subliming or intumescent material which is exposed to a hydrocarbon fire environment as defined by Underwriters
25 Laboratory procedure 1709 or a jet fire environment as defined by British Offshore Technology Report OTO 93 028. (21 December 1993). After cooldown, the samples were checked for "hand" retention, and results were recorded. The three item samples which were not embrittled were A-16, D-13, and E-16. All the most successful samples had been soaked at room
30 temperature for over twenty-four hours in an acid solution containing in excess

of 15% molal sulfuric acid, and two of the three samples had been soaked at room temperature for over twenty-four hours in the low-viscosity silicone emulsion.

Preliminary fire tests of the treated fiberglass fabric in a subliming fire-
5 protective coating system indicate that the system provides superior results.

To further test the treated fabrics, and to demonstrate their usefulness in composite materials, the material was embedded in small (approximately 10 cm square) test polypropylene sheets as follows. In separate tests, two active fire protective materials were applied to the fabric: a subliming material (Thermal
10 Science, Inc., THERMO-LAG 440-1) and a thin-film subliming and intumescent material (Thermal Science, Inc. THERMO-LAG 2000). Both these materials are flexible epoxy polysulfide based materials containing a subliming agent. They both swell and undergo an endothermic phase change when exposed to hyperthermal conditions. The materials are formulated to provide
15 different amounts of swelling. In each case, the active thermal protective material was thinned in a solvent or low viscosity resin diluent. The treated fiberglass fabric was placed in a container of the thinned material and squeezed in a wringer to remove excess coating. As shown in FIGS. 1 and 2, this produces a fabric 1 coated with material 3 to form a thermal protective structure
20 5. The coating 3 covers the fibers of the fabric 1 but does not close the individual cells in the fabric mesh, leaving openings 7. The coated fabric was heated to semicure the subliming material or to cure the intumescent material. The fiberglass remained somewhat elastic.

Polypropylene is a hard material with a surface that is difficult to adhere
25 to. As shown in FIGS 3-5, a molding process was utilized to embed the thermal protective structure 5 in a surface of a polypropylene sheet 11. The test square was heated to 200° to 210° C. The female portion 9 of a mold was heated to 60-70° C. The mold includes a ram with a platen 13 which is heated to 60-70° C. The thermoplastic square 11 was quickly placed into the mold with the
30 precoated fabric 5 on top of it, and the ram was be moved quickly to mold the

plastic before a skin is formed on the plastic. The sample was removed from the mold. This process caused the polypropylene to exude through the openings in the woven fabric and physically lock the fabric to the plastic sheet, so that part of the fabric 5 was embedded in the sheet and part remained visible at the surface of the sheet, as shown in FIG. 5. Comparative flame tests without reinforcement, with untreated fiberglass, with treated fiberglass, and with treated fiberglass coated with each of the active thermal protective materials showed that the treated fiberglass systems provided substantial increases in time to failure, and the coated fiberglass provided dramatic increases in time to failure. The thermal protective structure 5 was oriented on the flame side in the tests.

Based on the foregoing tests, it is believed that the treated fiberglass fiber of the present invention can be embedded into thermoplastic structures by the same process of incorporation during the molding process. Other fibers, coated with active thermal protective materials, can also be embedded into thermoplastic structures. Composite sheets including the treated and/or coated fabric may also be formed either by passing a single heated thermoplastic sheet and a sheet of the fabric between heated rollers, or by sandwiching the fabric between sheets of thermoplastic. In other embodiments, the coating of material on the fabric does close the individual cells and creates a continuous sheet of thermally protective structure which is bonded more easily to the surface of a substrate when the thermally protective structure is not embedded in the substrate.

A polypropylene trunk base, for use in holding the spare tire of an automobile at the bottom of an automobile trunk, is one example of a structure formed by the foregoing processes. Such a trunk base can be formed as an open rectangular box by embedding a fabric, including the treated fabric of the present invention or a fabric coated or impregnated with an active thermal protective material, into a polypropylene sheet as the sheet is formed into the trunk base. Alternatively, one or more polypropylene sheets can be formed into

composites before the molding operation. A polypropylene automotive fuel tank may be formed by the same methods, by forming the tank as two open shells and welding the shells together or by blow-molding the tank in a mold which is lined with a fabric that has been treated or precoated with an active thermal protective material.

Likewise, various automotive structures may be formed of felted natural fibers, such as linen fibers, and reinforced by embedding or otherwise securing to a face of the liner a fabric that has been precoated with an active thermal protective material. Such felted natural fiber sheets are preferably formed with an organic polymer adhesive or binder which holds the fibers together and which aids in holding the precoated fabric to the sheet when it is molded. The polymer binder softens at a temperature below the activation temperature of the active thermal protective material. For example, the binder may be activated at a temperature of about 200° C. and the active thermal protective composition may be activated at a temperature of 280°C. to 350°C.

An example of such a structure is a trunk liner. A portion of such a liner is shown in FIG. 6, in exploded form. The liner 21 is formed from two flexible batts 23 and 25 of flax strands coated with a thermally activated binder material with two thin polyethylene layers 27 sandwiched between them. Such trunk liners are known, a commercial version being produced by Thermoplast Company of Idstein, Germany. A decorative carpet 33 is placed on the free side of the batt 25, as is conventional. The composite is then molded and compressed by alternately hot pressing and cold pressing in a mold of suitable dimensions at suitable temperatures for suitable periods of time, as is known in the art. The pressing processes soften the binder and form a thinner, rigid, shell having a thickness of about seven millimeters.

The conventional liner is greatly improved by the use of a thermal protective structure 28 formed of a fiberglass mesh 29 precoated with FIRE-SORB 2001 (Nu-Chem, Inc., Fenton, Missouri, USA) flexible subliming intumescent thermal protective coating 31. The thermal protective structure 28

is formed from ordinary (E-glass) fiberglass coated with 600 to 800 grams per square meter of subliming material, to give a structure 28 about one-half millimeter thick. The coating covers the openings and forms a continuous film in this embodiment. The subliming material is an epoxy polysulfide which contains sublimers and other additives to make it flexible under the conditions of molding. The thermal protective structure 28 is laid over the batt 23. Optionally, a much thinner batt 35 of the flax material and binder is laid over the thermal protective structure 28. The protective structure 28 is laminated to the surface of the batt 23 using eighty bar pressure at a temperature of 220°C. for twenty seconds. When the thinner batt 35 is overlaid on the protective structure 28, the same molding conditions are used. In the molding process, the thermal protective structure 28 becomes adhered to the batt 23. Because the shell will be placed in an automotive trunk with the inner portion of the shell facing in the direction of the fuel tank, the thermal protective structure 28 is on the inside of the shell in this illustrative embodiment.

Tests of the liner structure 21 without the upper layer 35 show greatly lengthened times to failure when exposed to a 1,000°C. fire of controlled intensity. In the optional construction, the precoated mesh is hidden by the thin upper layer of compressed flax; under fire conditions, however, the upper layer quickly burns off and exposes the active thermal protective material. In both cases, the active protective material expands to about eight times its original thickness (eight mm from an initial half mm) while absorbing energy and producing an open cell matrix through which the sublimed gasses transpire, to provide a greatly extended time to failure of the structure. Preliminary tests indicate that a structure without the thermal protective structure 28 will fail under test conditions in less than forty-five seconds, while the protected structure of the present invention suffers little structural damage in over four minutes.

In applications where the structure is a container, the mesh is illustratively a single piece which extends across a lower side of the bottom and

up at least a part of the outside of an upstanding wall of the structure. In any of these cases, the present invention provides greatly extended times to failure in standard tests involving placing the thermoplastic container or other automotive structure over a standard fire and in other standard tests.

5 As variations within the scope of the appended claims will be apparent to those skilled in the art, the foregoing description is set forth only for illustrative purposes and is not meant to be limiting. For example, other types of fiberglass may be treated in accordance with the invention. Other combinations of acids may be utilized. The acid bath may include additives,
10 such as silicates for example. As previously noted, the time of acid or resin treatment may be reduced if the temperature of the bath is increased. Other silicones and other low viscosity organo-metallic resins than silicones may be utilized in the post-acid bath treatment of the fiberglass. The treated fiberglass may be used in other high-temperature systems. For example, a composite
15 material may be formed of at least one layer of thermoplastic having embedded therein fibers produced by the acid treatment method of the present invention. Also, a thermal protective composition may be produced having dispersed therein fibers produced by the acid treatment method of the present invention. Examples of such thermal protective compositions are a coating applied to a
20 substrate and a preformed self-supporting structure.

 The substrates of the composites of the invention may be formed of other polyolefins (such as polyethylene), other thermoplastics and even thermoset resins, and may be reinforced with various fibers. In the case of structures (mats) formed by pressing batts of fibers coated with adhesive
25 binders, the fibers are preferably natural (such as flax, hemp, or cotton), and the adhesive binder is also preferably recyclable. It will be understood that the binder may be activated by water or otherwise, rather than by heat, although heat-activated binders are presently greatly preferred. The substrate of the composite is preferably moldable into a sheet which is many times wider and
30 longer than its thickness, and the fabric is preferably adhered to the substrate

during the molding operation. It will be understood, however, that the composites may be formed by adhering the pretreated fabric to the substrate after the substrate is molded, although such a process is both slower and more complex than molding and adhering or embedding in a single step. The

5 composites may be formed into other structural containers and entirely other structures, such as other automotive elements (like package shelves and door facings), firewalls, and other high temperature barriers such as used on jet engines. The fabric to which the active thermal material is applied before being secured to the substrate is preferably fiberglass but may be other fabrics such as

10 those formed of threads or yarns of graphite, organic polymers (such as nylon, polyolefins, or acrylics), or natural fibers (like cotton or linen). The fabric may have a very loose weave (such as 0.5 openings per square centimeter) to a rather tight weave (such as thirty openings per square centimeter). The fabric is preferably a simple weave but may be knitted or woven in other known

15 manners. The fabric is precoated with an active thermal protective material which, when exposed to hyperthermal conditions, intumesces, sublimes, or preferably does both.

These variations are merely illustrative.

Claims

1. A method of treating fiberglass fiber to increase its resistance to heat, the method comprising treating the fiber with a mixture of acids comprising at least 15% sulfuric acid for a period sufficient to increase the softening point of the
5 fiber to at least 1000° C.
2. The method of claim 1 wherein the fiber is formed into a fabric before it is treated.
3. The method of claim 2 wherein the acid mixture further comprises at least one other mineral acid.
- 10 4. The method of claim 3 wherein the acid mixture comprises hydrochloric acid.
5. The method of claim 1 wherein the fiber is E-glass.
6. The method of claim 1 wherein the fiber is soaked in an acid bath for a period in excess of twenty-four hours.
- 15 7. The method of claim 2 comprising a further step of treating the fabric with a low viscosity resin after the acid treatment step.
8. The method of claim 7 wherein the resin is a silicone oil.
9. The method of claim 8 wherein the silicone oil is a water in oil emulsion.
- 20 10. A composite material comprising at least one layer containing a thermoplastic, the layer having embedded therein a fabric, the fabric being coated with an active thermal protective material selected from the group consisting of subliming materials and intumescent materials.
11. The composite of claim 10 wherein the fabric comprises an open weave
25 mesh having from 0.5 to 30 openings per square centimeter.
12. The composite of claim 10 wherein the fabric comprises fiberglass fiber having a softening point above about 850° C.
13. The composite of claim 10 wherein the active thermal protective material leaves openings in the weave of the fabric, the thermoplastic material
30 extending into the openings and forming a physical lock with the fabric.

14. A container formed of the composite of claim 10.
15. The container of claim 14 wherein the container is a structural automotive container selected from the group consisting of trunk bases and fuel tanks.
- 5 16. A structural automotive container comprising an open pan having a bottom and a peripheral upstanding wall, the pan being formed at least in part of an organic thermoplastic material having a fabric mesh embedded therein.
17. The container of claim 16 wherein the mesh is on a lower side of the bottom and the outside of the upstanding wall.
- 10 18. The container of claim 17 wherein the fabric mesh is a single piece of material extending across the bottom and up at least a part of the peripheral wall.
19. The container of claim 16 wherein the fabric comprises fiberglass fiber having a softening point above about 850° C.
- 15 20. The container of claim 19 wherein the fabric comprises fiberglass fiber having a softening point above about 1000° C.
21. The container of claim 20 wherein the fabric has been treated with a mixture of acids comprising at least 15% sulfuric acid.
22. The container of claim 16 wherein the container is a trunk base.
- 20 23. The container of claim 16 wherein the container is a fuel tank.
24. The container of claim 16 wherein the container is an inverted pan formed in part of thermoplastic-coated fibers, the fabric mesh being embedded in an inside surface of the pan.
25. A method of producing a structural automotive pan comprising
25 overlaying a thermoplastic sheet with a fabric cloth and thereafter forming the sheet into an open pan having a bottom and a peripheral upstanding wall and embedding the fabric in the thermoplastic sheet.
26. The method of claim 25 wherein the step of forming the sheet into an open pan and the step of embedding the fabric in the thermoplastic sheet are
30 performed simultaneously.

27. The method of claim 25 comprising a step of precoating the fabric with an active thermal protective material selected from the group consisting of subliming and intumescent materials.
28. A composite material comprising at least one layer of thermoplastic
5 having embedded therein a fabric produced by the method of claim 2.
29. A composite material comprising at least one layer of thermoplastic having embedded therein fibers produced by the method of claim 1.
30. A thermal protective composition having dispersed therein fibers produced by the method of claim 1.
- 10 31. In combination, a thermal protective material and a fiberglass fabric embedded therein, the fabric having been treated by the method of claim 2.
32. The combination of claim 31 wherein the thermal protective material is a coating applied to a substrate.
33. The combination of claim 31 wherein the thermal protective
15 composition is preformed into a self-supporting structure.
34. A method of protecting a substrate from fire or thermal extremes comprising applying to the substrate an uncured thermal protective material selected from the group consisting of intumescent materials and subliming materials, and thereafter a step of embedding in the thermal protective material
20 a fiberglass fabric produced by the method of claim 2.
35. A structure comprising an organic resin having embedded therein a fabric, the fabric being precoated with an active thermal protective material selected from the group consisting of subliming and intumescent materials.
36. The structure of claim 35 wherein the organic resin is a polyolefin.
- 25 37. A method of treating fiberglass fiber to give it superior high temperature resistance and texture, the method comprising treating the fiber with acid and thereafter soaking the fiber in a water-in-oil emulsion of low viscosity organo-metallic oil to fill pores in the glass.
38. The method of claim 37 wherein the low viscosity organo-metallic oil is
30 a low molecular weight silicone oil.

39. The method of claim 37 or 38 wherein the silicone is dimethyl polysiloxane.
40. The method of any one of claims 37-39 wherein the step of treating the fiber with acid comprises treating the fiber with a mixture of acids comprising at least 15% sulfuric acid for a period sufficient to increase the softening point of the fiber to at least 1000° C.
41. A method of forming a composite structure comprising a step of coating a fabric with an active thermal protective material selected from the group consisting of subliming and intumescent materials, a step of placing the coated fabric in a mold, and a step of forming a substrate into a shape in the mold containing the coated fabric.
42. The method of claim 41 wherein the substrate comprises a thermoplastic resin, the step of forming the substrate comprising heating the resin at least to a softening temperature, the coated fabric bonding to the softened resin.
42. The method of claim 41 wherein the resin comprises a polyolefin.
43. The method of claim 41 wherein the substrate is heated to a temperature below an activation temperature at which the active thermal protective material intumesces or sublimes.
44. The method of claim 41 wherein the fabric comprises fiberglass.
45. The method of claim 41 wherein the substrate comprises a felted material.
46. The method of claim 41 wherein the coated fabric includes windows therein, the substrate extending through the windows to lock the coated fabric to the substrate.
47. The method of claim 41 wherein the structure is an automotive trunk base, or trunk liner, or fuel tank.
48. A composite structure comprising a substrate, the substrate being formed at least in part of a thermoplastic material, and a thermal protective structure adhered to the substrate, the thermal protective structure comprising a fabric coated with an active thermal protective material, the thermal protective

material being selected from the group consisting of subliming and intumescent materials.

49. The structure of claim 48 wherein the thermal protective structure is adhered to the substrate by the thermoplastic material.

5 50. The structure of claim 48 wherein the thermal protective structure is embedded in the thermoplastic material.

Claims

1. A method of treating fiberglass fiber to increase its resistance to heat, the method comprising treating the fiber with a mixture of acids comprising at least 15% sulfuric acid for a period sufficient to increase the softening point of the fiber to at least 1000° C.
2. The method of claim 1 wherein the fiber is formed into a fabric before it is treated.
3. The method of claim 2 wherein the acid mixture further comprises at least one other mineral acid.
4. The method of claim 3 wherein the acid mixture comprises hydrochloric acid.
5. The method of claim 1 wherein the fiber is E-glass.
6. The method of claim 1 wherein the fiber is soaked in an acid bath for a period in excess of twenty-four hours.
7. The method of claim 2 comprising a further step of treating the fabric with a low viscosity resin after the acid treatment step.
8. The method of claim 7 wherein the resin is a silicone oil.
9. The method of claim 8 wherein the silicone oil is a water in oil emulsion.
10. A composite material comprising at least one layer containing a thermoplastic, the layer having embedded therein a fabric, the fabric being coated with an active thermal protective material selected from the group consisting of subliming materials and intumescent materials.
11. The composite of claim 10 wherein the coated fabric comprises an open mesh having from 0.5 to 30 openings per square centimeter, the thermoplastic in the layer extending into the openings and forming a mechanical lock with the coated fabric.
12. The composite of claim 10 wherein the fabric comprises fiberglass fiber having a softening point above about 850° C.

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13. The composite of claim 10 wherein the active thermal protective material leaves openings in the weave of the fabric, the thermoplastic material extending into the openings and forming a physical lock with the coated fabric.
14. A container formed of the composite of claim 10.
- 5 15. The container of claim 14 wherein the container is a structural automotive container selected from the group consisting of trunk bases and fuel tanks.
16. A structural automotive component having a bottom and an upstanding wall, the pan being formed of the composite material of claim 10.
- 10 17. The component of claim 16 wherein the mesh is on a lower side of the bottom and the outside of the upstanding wall.
18. The component of claim 17 wherein the fabric mesh is a single piece of material extending across the bottom and up at least a part of the upstanding wall.
- 15 19. The component of claim 16 wherein the fabric comprises fiberglass fiber having a softening point above about 850° C.
20. The component of claim 19 wherein the fabric comprises fiberglass fiber having a softening point above about 1000° C.
21. The component of claim 20 wherein the fabric has been treated with a
- 20 mixture of acids comprising at least 15% sulfuric acid.
22. The component of claim 16 wherein the component is a trunk base.
23. The component of claim 16 wherein the component is a fuel tank.
24. The component of claim 16 wherein the component is an inverted pan, formed in part of thermoplastic-coated fibers, the fabric mesh being embedded
- 25 in an inside surface of the pan.
25. A method of forming a composite structure comprising a step of coating a fabric with an active thermal protective material selected from the group consisting of subliming and intumescent materials, and thereafter a step of softening a resin component of a substrate and embedding the coated fabric in
- 30 the softened resin.

26. The method of claim 25 wherein the substrate is a sheet, and wherein the sheet and the fabric are formed into a structure simultaneously with the step of embedding the fabric in the sheet.
27. The method of claim 25 wherein the active thermal protective material
5 leaves openings in the weave of the fabric, the softened resin extending into the openings and forming a physical lock with the coated fabric.
28. A composite material comprising at least one layer of thermoplastic having embedded therein a fabric produced by the method of claim 2.
29. A composite material comprising at least one layer of thermoplastic
10 having embedded therein fibers produced by the method of claim 1.
30. A thermal protective composition having dispersed therein fibers produced by the method of claim 1.
31. In combination, a thermal protective material and a fiberglass fabric embedded therein, the fabric having been treated by the method of claim 2.
- 15 32. The combination of claim 31 wherein the thermal protective material is a coating applied to a substrate.
33. The combination of claim 31 wherein the thermal protective composition is preformed into a self-supporting structure.
34. A method of protecting a substrate from fire or thermal extremes
20 comprising applying to the substrate an uncured thermal protective material selected from the group consisting of intumescent materials and subliming materials, and thereafter a step of embedding in the thermal protective material a fiberglass fabric produced by the method of claim 2.
35. A structure comprising an organic resin having embedded therein a
25 fabric, the fabric being precoated with an active thermal protective material selected from the group consisting of subliming and intumescent materials.
36. The structure of claim 35 wherein the organic resin is a polyolefin.
37. A method of treating fiberglass fiber to give it superior high temperature resistance and texture, the method comprising treating the fiber with acid and

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thereafter soaking the fiber in a water-in-oil emulsion of low viscosity organo-metallic oil to fill pores in the glass.

38. The method of claim 37 wherein the low viscosity organo-metallic oil is a low molecular weight silicone oil.

5 39. The method of claim 38 wherein the silicone is dimethyl polysiloxane.

40. The method of claim 37 wherein the step of treating the fiber with acid comprises treating the fiber with a mixture of acids comprising at least 15% sulfuric acid for a period sufficient to increase the softening point of the fiber to at least 1000° C.

10 41. A method of forming a composite structure comprising a step of treating a fabric with an active thermal protective material selected from the group consisting of subliming and intumescent materials, a step of placing the treated fabric in a mold, and a step of forming a substrate into a shape in the mold containing the treated fabric.

15 42. The method of claim 41 wherein the substrate comprises a thermoplastic resin, the step of forming the substrate comprising heating the resin at least to a softening temperature, the treated fabric bonding to the softened resin.

43. The method of claim 41 wherein the substrate is heated to a temperature below an activation temperature at which the active thermal protective material
20 intumesces or sublimes.

44. The method of claim 41 wherein the fabric comprises fiberglass.

45. The method of claim 41 wherein the substrate comprises a felted material.

46. The method of claim 41 wherein the coated fabric includes windows
25 therein, the substrate extending through the windows to lock the coated fabric to the substrate.

47. The method of claim 41 wherein the structure is an automotive trunk base, or trunk liner, or fuel tank.

48. The method of claim 41 wherein the resin comprises a polyolefin.

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49. A composite structure comprising a substrate, the substrate being formed at least in part of a thermoplastic material, and a thermal protective structure adhered to the substrate, the thermal protective structure comprising a fabric coated with an active thermal protective material, the thermal protective material being selected from the group consisting of subliming and intumescent materials, the substrate adhering chemically and mechanically to the pretreated mesh fabric.

50. The structure of claim 49 wherein the thermal protective structure is adhered to the substrate by the thermoplastic material.

51. The structure of claim 49 wherein the thermal protective structure is embedded in the thermoplastic material.

52. A composite structure comprising a substrate, the substrate being formed at least in part of a polyolefin, and a mesh fabric treated with an active thermal protective material, the thermal protective material being selected from the group consisting of subliming and intumescent materials, the treated mesh fabric having from 0.5 to 30 openings per square centimeter, the resin adhering chemically and mechanically to the pretreated mesh fabric.

53. The structure of claim 52 wherein the polyolefin is polypropylene.



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NOTE: The following information concerns the steps which you are required to take for entry into the regional phase before the EPO. You are strongly advised to read it carefully. Failure to take the appropriate steps in due time could lead to the application being deemed withdrawn.

1. European patent application no. 98935744.7 has been allotted to the above-mentioned international patent application.
2. Applicants having neither a residence nor their principal place of business within the territory of one of the EPC Contracting States may initiate the regional (European) processing of the international application themselves, provided they do so before expiry of the 21st or 31st month as from the priority date (see Legal Advice of the EPO no. 18/92 published in OJ EPO 1992, 58).

Note, however, that such applicants must be represented in the regional phase before the EPO as designated or elected Office by a professional representative whose name appears on the EPO list of representatives (Arts. 133(2) and 134(1) EPC).

After expiry of the 21st or 31st month, any procedural steps which are taken by the representative of the applicant in the international phase, who is not, however, entitled to practise before the EPO, will have no effect and will, thus, result in loss of rights.

The appointment of a professional representative entitled to practise before the EPO is possible/advisable at an early stage during the international phase (any time after the 14th month from the priority date) in view of representing applicants before the EPO as designated or elected Office.

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